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ORIGINAL ARTICLE

Chemical interaction of the GaAs, GaSb, InAs, and InSb single crystals surface with I_2 + DMF (methanol) etchants

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Abstract

The nature of the chemical dissolution of GaAs, GaSb, InAs, and InSb single crystals in I_2 + dimethylformamide (DMF) and I_2 + methanol solutions under reproducible hydrodynamic conditions has been studied. The dependence of the dissolution rate of these semiconductors on the composition of etchants, stirring rate, temperature, and storage time has been investigated. The compositions of polishing, selective and non-polishing solutions have been determined. The state of the surface after chemical-dynamic polishing (CDP) was investigated by metallographic analysis, X-ray Photoelectron Spectroscopy (XPS), and atomic force microscopy (AFM). The compositions of etchants and the modes of carrying out the CDP process for the mentioned above semiconductors were optimized.

Keywords Chemical-dynamic polishing · Iodine-containing etchant · Dissolution rate · Surface morphology · Polishing solution

Introduction

Bromine solutions in various organic and inorganic solvents are most widely used for the chemical treatment of III–V semiconductors. As a result of etching with such solutions, bromides are formed that are readily soluble in water and organic solvents. Among organic compounds, the following reagents are used as bromine solvents: methanol, ethanol, ethylene glycol, dimethylformamide, etc.; therefore, such mixtures are also often referred to as bromine-containing etchants.

The dissolution rate and surface quality of the samples after etching strongly depend on the concentration of bromine in methanol. Polishing region for InAs is in the region 1.5–2.0 vol.% Br_2 (4–6 μm·min^{-1}, $R_z \sim 0.07$ μm), and for GaAs in the region 2.5–3.0 vol.% Br_2 (3.5–4.6 μm·min^{-1}, $R_z \sim 0.08$ μm) (Perevoshchikov 1995). The reaction rate is significantly affected by the mixing of the solution, which is especially noticeable at low concentrations of bromine in methanol ($T = 293$ K). As a result, the dissolution processes of InAs and GaAs in the aforementioned solutions proceed in the field of mixed kinetics. In the work (Klem et al. 1991), the authors found that surface treatment of InSb (100) plates with etching solutions of Br_2 + methanol, even at very low concentrations of bromine, leads to the formation of very poor quality surface morphology. As a result of chemical–mechanical polishing (CMP) treatment of GaAs with a $Br_2 + CH_3OH$ solution, the surface was depleted in arsenic to the atomic ratio: As/Ga = 0.7 (Contour et al. 1985). To detect dislocations on the surface of GaSb, a 3% solution of Br_2 in methanol was used; triangular etching pits are formed only on the (111)A surface (Costa et al. 1997).

The authors (Vozmilova and Berdichenko 1980) used an anisotropic etchant containing 5 vol.% Br_2 in DMF to investigate *n*-GaAs (without stirring at room temperature, $v = 2.4$ μm·min^{-1}). It was found that the dissolution rate linearly depends on the bromine concentration, and the (111) A plane has the lowest etching rate. The etching rate of these wafers in a solution of 5 vol.% Br_2 in methanol was 6 μm·min^{-1} (anisotropic etchant). To achieve the required viscosity of the Br_2 + DMF solution, glycerol was added to the etchant (Starovoitova and Sannikov 1980) and the dissolution of *p*- and *n*-type single crystals of InSb with {211} orientation in this solution was studied. The etching rate of InSb weakly depends on temperature, and the process proceeds according to the diffusion mechanism ($E_a = 13–17$ kJ·mol^{-1}). Optimal mode for this process is as

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follows: $T = 338$ K; rotation speed, 50–100 min^{-1}; DMF/glycerol/Br_2 ratio = 60:5:2. An etchant of the same composition was used for pretreatment of *n*-InSb samples with the {211}B orientation, as well as for *n*- and *p*-InAs with the {111}B orientation, grown by the Czochralski method (Davydov et al. 1987).

In addition to the above bromine-containing etchants, bromine-evolving etchants are also used, in which bromine is released during the interaction of the starting reagents. When comparing bromine-evolving etchants $H_2O_2 + HBr$ and $(NH_4)_2Cr_2O_7 + HBr$ (Table 1), it can be seen that solutions based on ammonium dichromate form a polished surface with much better roughness parameters. After treatment with etchants based on $(NH_4)_2Cr_2O_7 + HBr$ (Levchenko et al. 2022), the surface of InSb crystals is close to stoichiometric with a slight enrichment in In (atomic ratio In/Sb = 1.03). Kusiak (2002) gives data on the roughness parameters of InAs (111) crystals after CDP with bromine-evolving etchants: for example, after etching with $HNO_3 + HBr + C_3H_8O_3$, the value of $\boldsymbol{R_z} = 0.178$ µm; after etching with $H_2O_2 + HBr + C_6H_8O_7$—$\boldsymbol{R_z} = 0.061$ µm, and after treatment with a $K_2Cr_2O_7 + HBr + C_3H_6O_3$ solution, $\boldsymbol{R_z} = 0.015$ µm (data obtained using a profilometer). The authors (Tomashyk et al. 2020) polished single crystals of GaAs, InAs, InAs (Sn), GaSb and InSb in etching compositions $H_2O_2 + HBr +$ tartaric acid at a CDP rate of 2–13 µm·min^{-1}; in this case, a surface was formed with R_a values of 10–20 nm.

Iodine looks like a more promising candidate compared to bromine, since it is characterized by half the redox potential ($Br_2/2Br^- = 1.09$ V, $I_2/2I^- = 0.54$ V) and, therefore, is a weaker oxidizing agent. It is expected that the etch rate of III-V semiconductors will be slower and better controlled, and the etching process will result in highly polished surfaces with satisfactory roughness parameters and surface chemistry compared to bromine-containing and bromine-evolving solutions. Iodine-based etchants are less toxic and have a relatively high polishing quality; moreover, such etchants are more stable during exposure, since they retain a constant concentration of dissolved iodine in the solution longer. Thus, the etchant of I_2 in methanol turned out to be useful for etching InSb (Fuller and Allison 1962), but experimental studies are not presented in the work.

The above advantages make it possible to recommend such etchants for chemical polishing of GaAs, GaSb, InAs, and InSb surfaces and for controlled removal of thin layers from the surface of single crystals, while maintaining high polishing quality. Systematic studies of the chemical treatment of GaAs, GaSb, InAs, and InSb semiconductor wafers in $I_2 +$ DMF and $I_2 +$ methanol etching solutions have not been carried out, but our previous studies have shown the promise of using such etchants for their CDP and selective etching.

The purpose of this work is to experimentally study the regularities of the CDP of InAs, InSb, GaAs, and GaSb single crystals by etchants based on $I_2 +$ DMF and $I_2 +$ methanol solutions and to study the kinetics and establish the limiting stages of the dissolution process, determine the surface quality by metallographic microscopy, AFM, XPS, as well as optimize polishing compositions at the formation of high-quality surfaces of these semiconductor materials.

Experimental procedures

For experimental studies, *n*-type semiconductor crystals were used: GaAs (111), GaSb (112), InAs (001), and InSb (112). Single crystals were cut into 5 mm × 5 mm (square was 25 mm^2) plates with the thickness of 2 mm in size

Table 1 Roughness parameters of GaAs, GaSb, InAs, and InSb single-crystal wafers (AFM method) after CDP and CMP treatment with polishing etchants (Tomashik et al. 2012; Levchenko et al. 2018; Levchenko et al. 2022)

Material	Treatment	Etchant compositions	R_a (nm)	*Rms* (nm)
GaAs (100)	CMP	$H_2O_2 + HBr + EG$	14.8	18.9
	CMP + CDP	$H_2O_2 + HBr + EG$	10.5	13.2
GaAs (111)	CMP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.1	0.2
GaSb (112)	CMP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.4	0.6
InAs (100)	CMP	$H_2O_2 + HBr + EG$	12.7	15.7
	CMP + CDP	$H_2O_2 + HBr + EG$	18.9	23.0
	CMP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.2	0.2
	CMP + CDP	$(NH_4)_2Cr_2O_7 + HBr$	3.2	4.0
	CMP + CDP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.3	0.5
InSb (211)	CMP	$H_2O_2 + HBr + EG$	12.5	16.5
	CMP + CDP	$H_2O_2 + HBr + EG$	11.2	14.4
InSb (112)	CMP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.3	0.5
	CMP + CDP	$(NH_4)_2Cr_2O_7 + HBr$	1.1	1.4
	CMP + CDP	$(NH_4)_2Cr_2O_7 + HBr + EG$	0.3	0.3

Table 2 The elimination rate of the GaAs, GaSb, InAs, and InSb surfaces layer during mechanical treatment with free abrasives

Semiconductor	The elimination rate of the surface layers, $\mu m \cdot min^{-1}$	
	ASM 5/3	ASM 1/0
GaAs (111)	~ 100	~ 13
GaSb (112)	~ 70	~ 8
InAs (001)	~ 70	~ 6
InSb (112)	~ 7	~ 3

Table 3 The range of values of the damaged layer of the GaAs, GaSb, InAs, and InSb after various types of machining (Perevoshchikov 1995)

Semiconductor	Depth of a structurally disturbed layer, μm		
	After cutting	ASM 5/3	ASM 1/0.5
GaAs	34–75	11–18	5–9
GaSb	60–95	11–19	6–12
InAs	50–95	11–18	4–11
InSb	100–200	25–35	15–20

using wire cutting, which were then glued with picein with the non-working side onto quartz substrates. The residual picein was removed with an organic solvent.

Processing of plates consisted of the following stages: mechanical grinding, chemical–mechanical polishing and chemical-dynamic polishing. The disturbed layer formed during the cutting process was partially removed by mechanical grinding using aqueous suspensions of diamond abrasive powders of the brands ACM 10/7 (grain size 10–7 μm), ACM 5/3 (grain size 5–3 μm) and ACM 1/0 (< 1 μm). Each stage of mechanical grinding was carried out on a glass polisher with powders in the order of decreasing diameter of the abrasive grain. The elimination rate of the surface layers is different depending on the nature of the materials and abrasive grit (Table 2). The damaged layer of ~ 150 μm thick was removed.

The depth of the damaged layer for the investigated semiconductor wafers is given in Table 3: it is seen, that the depth of the damaged layer increases for with decreasing the microhardness: $H_{GaAs} > H_{GaSb} > H_{InAs} > H_{InSb}$ (Perevoshchikov 1995).

Removal of mechanical contaminants (remains of suspensions, dust, and so on) was carried out according to the following rinsing scheme:

Solution of surfactants → H_2O(dist.) → H_2O(dist.) → H_2O(dist.)

The cleaned plates were dried in a stream of dry air. After mechanical processing, the crystal surface remains structurally imperfect.

Chemical–mechanical polishing reduces crystal deformation to minimum values. The CMP process was carried out on a cloth-covered glass polisher using a polishing solution (a universal bromine-evolving etchant) developed in our laboratory by Levchenko et al. (2022). The CMP process was conducted at $T = 293–295$ K, the etchant was constantly fed at a rate of 2–3 $mL \cdot min^{-1}$, and a pressure on the plates was 2–3 kPa at $\gamma = 90\ min^{-1}$.

Chemical-dynamic polishing of crystals contributes to obtaining a nano-sized relief. CDP of GaAs, GaSb, InAs, and InSb substrates was carried out using I_2 + DMF (methanol) etching solutions. Etching mixtures were prepared from the following initial reagents: elemental crystalline I_2, DMF, and methanol (all reagents of pure grade).

The investigation of the CDP of GaAs, GaSb, InAs, and InSb plates was carried out under reproducible hydrodynamic conditions using the rotating disk technique on the CDP installation at $T = 296 - 300$ K and the speed of the disk rotation $\gamma = 78\ min^{-1}$ for $3 - 5$ min (20 min for GaAs). The use of this technique contributes to the constant arrival of fresh portions of the etchant to the surface of the crystals and the removal of the products of their interaction. It also allows determining the kinetic laws of the semiconductor dissolution process, in particular, the limiting stages of the general etching process, and helps to exclude the influence on the nature of the dissolution of such side effects as passivation and catalysis.

The speed of removal of the disturbed layer was determined using the electronic indicator TESA DIGICO 505 MI with accuracy ± 0.2 μm. The thickness measurements were performed before and after the CDP at several points on the crystal surface at once on 4 samples. After chemical treatment, semiconductor wafers must be immediately removed from the etching solution and washed according to the following scheme (the duration of washing in each solution is 1 min):

$Na_2S_2O_3$(1.4M.) → H_2O(dist.) → 15% NaOH → H_2O(dist.) → H_2O(dist.)

The microstructure of the surface of the samples after etching was studied in white light using a metallographic microscope MIM-7 with a digital video camera eTREK DCM800 (8Mpix) at a magnification of 25 × to 1600 × and optical microscope NU-2E (Carl Zeiss) at a magnification of 50 × to 1250 ×. The parameters of the surface roughness were measured using a profilometric analysis by the mechanical contact method on a base length of 0.25 mm (tracing length of 1.5 mm and tracing rate of 0.15 $mm \cdot s^{-1}$) using a HOMMEL-ETAMIC W5 profilometer, which allows determining the height of micro-uniformities ≥ 5 nm in the measurement range − 210/+ 110 μm (DIN 4772 class 1 accuracy—3%). Morphological studies of the polished surfaces were carried out by the AFM method using a

NanoScope IIIa Dimension 3000 microscope (Digital Instruments, USA) in periodic contact mode at room conditions with the use of NCH serial silicon probes with a nominal tip radius of up to 10 nm (NanoWorld).

The composition of the surface of single-crystal plates GaAs, GaSb, InAs, and InSb after chemical treatment was studied by X-ray photoelectron spectroscopy. The X-ray photoelectron spectroscopy (XPS) analysis was carried out by using a PHI5600 spectrometer with a monochromatic Al K_α source. The work function and linearity adjustments were made using Au $4f_{7/2}$ (BE 84 eV) and Cu $2p_{3/2}$ (BE 932.6 eV) peaks. The measurements were carried with and without surface cleaning by etching with Ar^+ ions with energy of 5 keV.

Results and discussion

The chemical dissolution of the GaAs, GaSb, InAs, and InSb single crystals was studied in the concentration range of 6–18 mass.% I_2 in DMF at $T = 296$ K and disk rotation speed $\gamma = 78$ min^{-1}. The dependces of the etching rate of the above plates on the concentration of I_2 solutions in DMF are presented in Fig. 1. As can be seen from the figure, with an increase in the amount of I_2 in DMF, the dissolution rate for InSb, InAs and GaSb crystals increases within the range of 0.4–7.7 μm·min^{-1}, 0.5–3.3 μm·min^{-1} and 1.2– 5.0 μm·min^{-1}, respectively, while for GaAs, the etching rates do not change significantly and do not exceed 0.2 μm·min^{-1}. The polishing regions of solutions for InSb is in the range of 9–18 mass.% I_2 in DMF, for GaSb, the entire studied range turned out to be polishing, and solutions containing 9–18 mass.% I_2 in DMF are also selective (pits are formed on the shiny polished surface at the single crystals etching). For InAs (the content of I_2 is 6 and 18 mass.%) and GaAs (the content of I_2 is 9 and 18 mass.%), a semitransparent film is visible on the polished surface, while all other etchant compositions are non-polishing.

To study the concentration dependences of the etching rate of GaAs, GaSb, InAs, and InSb plates, compositions with a content of 3–15 mass.% I_2 in methanol ($T = 298$ K, $\gamma = 78$ min^{-1}) were chosen. Figure 2 shows that with an increase in the amount of I_2 in methanol to 12 mass.%, the dissolution rate of InSb crystals increases within the range of 1.9–9.6 μm·min^{-1}, and with a further increase in the concentration of I_2, it decreases to 1.4 μm·min^{-1}. For InAs plates in the entire range of concentrations, the etching rate increases from 1.4 to 5.9 μm·min^{-1}. In the case of GaSb, the dissolution rate increases by 0.9–5.2 μm·min^{-1} in the concentration range of 3–9 mass.% I_2 in methanol, and after further increasing the I_2 content, it decreases to 1.6 μm·min^{-1}. For GaAs samples for some etchant compositions, the CDP rates do not exceed 0.8 μm·min^{-1}. The range of polishing solutions for InSb is within 3–12 mass.% I_2 in methanol, and for GaSb—3–9 mass.% I_2 in methanol, in addition to polishing properties, these etchants also have selective properties; for InAs, all solutions are non-polishing (at an I_2 content of 9 mass.%, a translucent film is visible on the polished surface), while for GaAs, the surface is polished and mirror-like in the entire range of the investigated solutions. The surface of GaAs in solutions of 6 and 9 mass.% I_2 + methanol is not etched, but remains polished and mirror-like. This may be due to the passivation of the surface by the products of the interaction of the etching composition with the semiconductor.

To understand the processes that occur during the dissolution of InSb and GaSb in etching compositions I_2 + DMF and I_2 + methanol, kinetic studies were conducted and the dependence of the dissolution rate (v) on

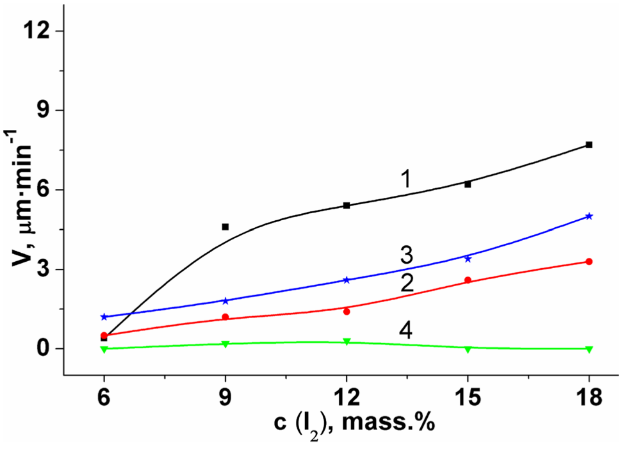

Fig. 1 Concentration dependences of the dissolution rate for **(1)** InSb, **(2)** InAs, **(3)** GaSb and **(4)** GaAs crystals in I_2 + DMF solutions ($T = 296$ K, γ = 78 min.$^{-1}$)

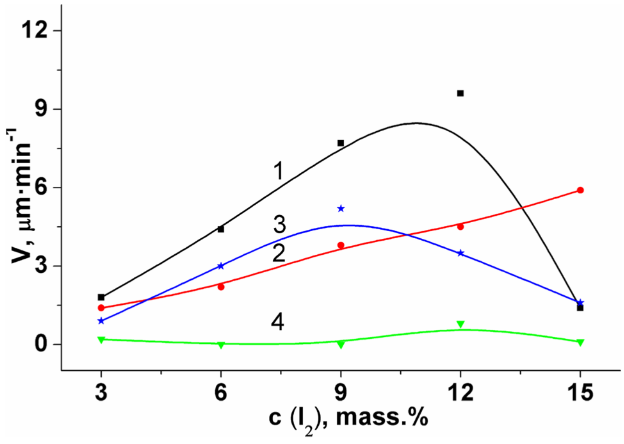

Fig. 2 Concentration dependences of the dissolution rate for **(1)** InSb, **(2)** InAs, **(3)** GaSb and **(4)** GaAs crystals in I_2 + methanol solutions ($T = 298$ K, γ = 78 min.$^{-1}$)

the disk rotation speed was plotted in the coordinates $v^{-1} - \gamma^{-1/2}$ ($\gamma = 32$–116 min^{-1}) at $T = 294$ K and 300 K, as well as on the etching temperature in coordinates $\ln v - 1/T$ ($T = 285$–307 K) at $\gamma = 78$ min^{-1}. Graphical construction of such dependencies allows to determine the nature of the processes taking place during the dissolution of semiconductors, and to find out which stage (diffusion or kinetic) is limiting and limits the speed of the heterogeneous dissolution process. The reaction rate of the heterogeneous interaction between the surface of the crystal and the etching solution is described by the equation: $v^{-1} = 1/kC_o + (a/DC_o)\,\gamma^{-1/2}$, where k is the reaction rate constant, C_o is the concentration of the active component, D is the diffusion coefficient of the component in solution, and a is a constant (Perevoshchikov 1995; Luft et al. 1982). With diffuse limitation of the dissolution process, $k >> 0$ and the first term of the equation becomes equal to zero, so the dependence $v^{-1} - \gamma^{-1/2}$ is directed to the origin of coordinates. With a mixed mechanism of the process, extrapolation of a straight line cuts off a segment on the Y axis equal to $1/kC_o$. If the process is limited by the chemical reaction, then $DC_o >> a$, already the second term of the equation is equal to zero, and the dependence becomes parallel to the abscissa axis. As can be seen from Fig. 3a and b for InSb and GaSb semiconductor wafers, the corresponding lines can be extrapolated to the origin of coordinates, from which it can be concluded that the dissolution mechanism is limited by diffusion stages.

The temperature dependence of the dissolution rate is described by the Arrhenius equation: $k = C_E e^{-Ea/RT}$, where k is the rate constant of the chemical reaction, C_E is the pre-exponential factor (particle collision frequency), E_a is the apparent energy of the activation process, and R is the universal gas

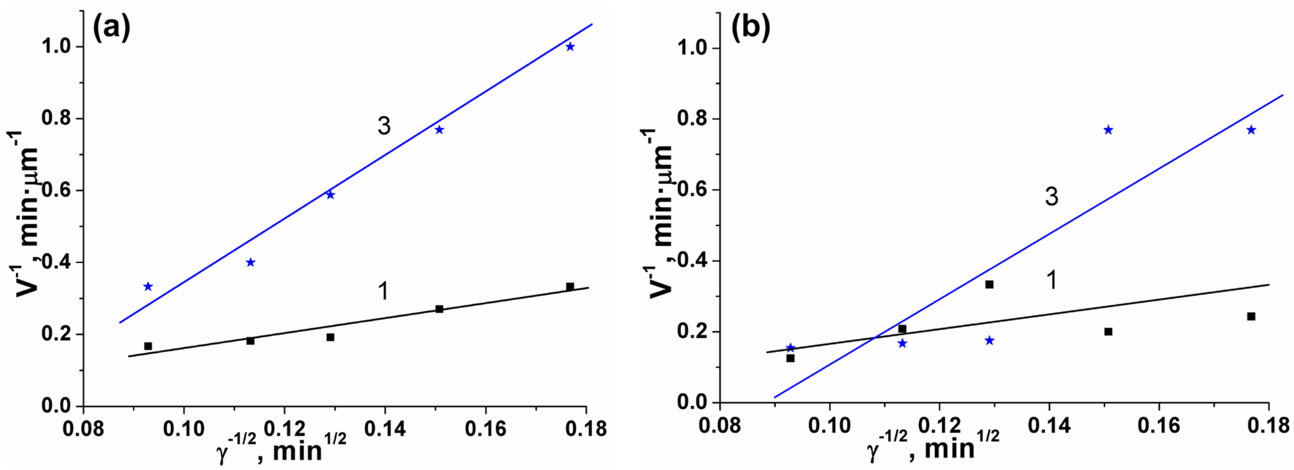

Fig. 3 Dependences of the dissolution rate v (μm·min^{-1}) of InSb (**1**) and GaSb (**3**) single-crystal plates on the speed of the disk rotation in etchant solutions of 9 mass.% I_2 in DMF (**a**) at $T = 300$ K and 9 mass.% I_2 in methanol (**b**) at $T = 294$ K

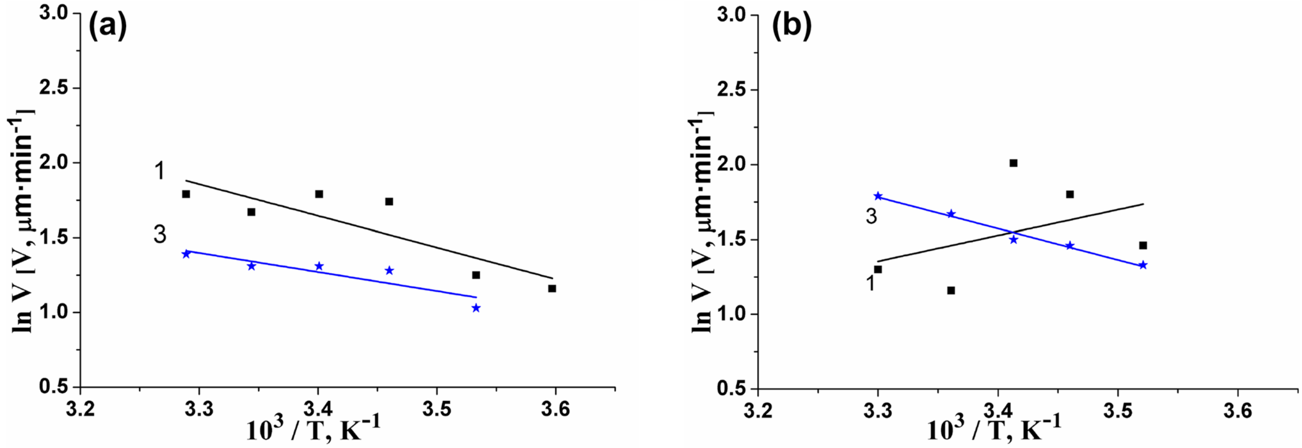

Fig. 4 Dependences of the dissolution rate (μm·min^{-1}) on the temperature of the solutions of (**a**) 9 mass.% I_2 in DMF and (**b**) 9 mass.% I_2 in methanol: **1**—InSb; **3**—GaSb ($\gamma = 78$ min^{-1})

constant. Figure 4a and b shows the dependence of the dissolution rate of the semiconductors on the temperature in the solution of 9 mass.% I_2 in DMF (or methanol). The calculated apparent activation energy (**E_a**) and the logarithm of the pre-exponential factor (**ln C_E**) are given in Table 4. It should be noted that with an increase in the temperature of the etchant 9 mass.% I_2 in methanol above 297 K, the etching rate of InSb wafers (Fig. 4b, line 1) decreases, and a relief surface is formed; it is obvious that the dissolution mechanism is not diffuse. The difference between the obtained results can be explained as follows: either a mixed dissolution mechanism in which diffusion processes prevail, or the InSb surface is partially passivated with increasing temperature, so the dissolution rate is slightly dependent on temperature.

As can be seen from Table 4, the calculated values of **E_a** of the dissolution process of the investigated single crystals did not exceed 30 kJ·mol^{-1} in all cases, that is, they do not exceed the permissible value for diffusion-controlled chemical processes (Perevoshchikov 1995). This confirms the conclusion about the diffuse mechanism of dissolution of these materials (Sangwal 1987).

The surface state of the GaAs, GaSb, InAs, and InSb single crystals after CDP with etching compositions I_2 + DMF (methanol) was studied by metallographic and profilometric analyses, AFM, and XPS. Figure 5a illustrates the microstructure of the surface of GaSb wafers after CDP with an etching solution of 9 mass.% I_2 in methanol ($T = 290$ K); at this temperature, a matte surface is formed. The image shows pyramidal etch pits, as well as clusters of structural defects. At a temperature $T = 288$ K and below, a pit-like relief “lemon peel” is formed on the GaSb surface (Fig. 5b).

In Fig. 6 shows the microstructure of the GaAs (111) surface after chemical etching with a solution of I_2 + DMF (non-polishing etching agent, the surface is characterized by a metallic luster).

Table 5 summarizes the surface roughness parameters (R_z) of the GaAs, GaSb, InAs, and InSb wafers after cutting and subsequent grinding with free diamond abrasives. The measurements were performed over a base length of 0.25 mm at a tracing length of 1.5 mm.

The AFM method was used to examine only the polished surfaces after the CDP with a mirror-like shine characteristic. Figure 7 presents a 3D image of the GaAs plate surface.

The data obtained indicate that the *Rms* value of the polished surface of GaAs crystals does not exceed 1.0 nm (Table 6). After surface treatment of GaAs crystals with etching solutions of I_2 in methanol, the roughness parameters meet the requirements for ultrasmooth polished surfaces and do not exceed 10 nm (Pop and Sharodi 2001).

XPS analyses were carried out after chemical treatment in I_2 + DMF and I_2 + methanol (samples were exposed to

Table 4 The pre-exponential factor (**ln C_E**) and the apparent activation energy (**E_a**) of the dissolution process of GaSb, InAs, and InSb plates in a solution of 9 mass.% I_2 in DMF (methanol)

Semiconductor	The composition of the etchant					
	9 mass.% I_2 in DMF			9 mass.% I_2 in methanol		
	ln **C_E**	**E_a**, kJ·mol^{-1}	Mechanism of dissolution	ln **C_E**	**E_a**, kJ·mol^{-1}	Mechanism of dissolution
GaSb	5.6	10.6	Diffusion	8.7	17.4	Diffusion
InSb	8.8	17.6	Diffusion	–	–	Mixed

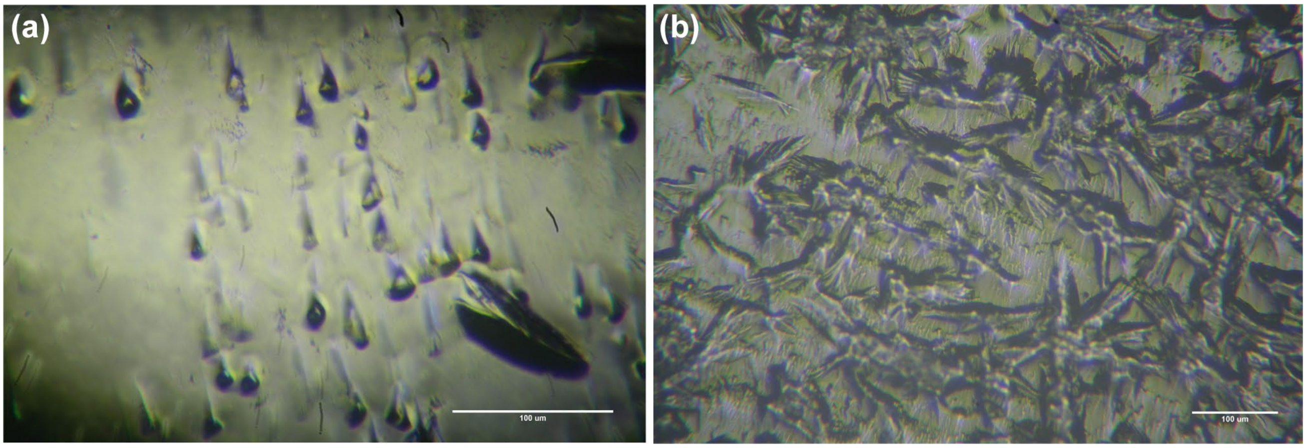

Fig. 5 Microstructure of the surface of GaSb (112) after CDP with a solution of 9 mass.% I_2 in methanol at $T = 290$ K (**a**) and $T = 288$ K (**b**) (optical microscope NU-2E)

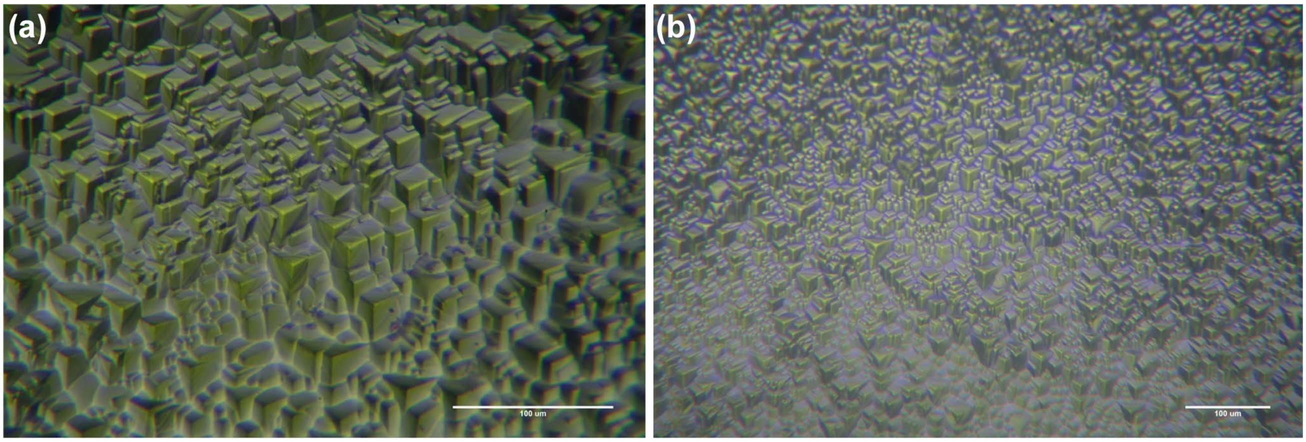

Fig. 6 The microstructure of the GaAs (111) surface after CDP with a solution of 9 mass.% I_2 in DMF (optical microscope NU-2E)

Table 5 The GaAs, GaSb, InAs, and InSb surface roughness parameters after different mechanical processing (HOMMEL-ETAMIC W5 profilometer)

Processing step	R_z, μm				Surface condition[a]
	InSb	InAs	GaSb	GaAs	
Wire saw cutting	1.3	3.5	2.1	2.5	Wavy, rough surface with cutting traces (longitudinal scratches, small steps)
Wire saw cutting + grinding with free ASM 10/7 abrasive	3.1	3.6	2.9	2.8	Dull, rough surface with structural defects
Wire saw cutting + grinding with free ASM 10/7 + ASM 5/3 abrasives	1.7	1.6	1.3	1.4	
Wire saw cutting + grinding with free ASM 10/7 + ASM 5/3 + ASM 1/0 abrasives	0.3	0.3	0.4	0.3	

R_z is the sum of the average magnitudes of the heights of the five highest elevations file and the depths of the five lowest depressions in the surface profile;

[a] MIM-7 with an eTREK DCM800 digital video camera (8 Mpix)

air for more than 2 h after CDP) and after ion etching (Tables 7 and 8). It was found that for GaSb and GaAs the atomic ratio V/III tends to values of > 1 after all types of treatments. This means that the surface is always enriched in Sb or As for GaSb and GaAs, respectively. XPS analysis showed that if the washing conditions are observed (Table 7), only the oxide phases of the V elements are presented on the surface. This corresponds to the formation of native oxide on the surface of the samples. Traces of carbon, iodine, and Na were also detected on the surface, but their concentration did not exceed 1 at.% (except for C due to accidental carbon). Also, the analysis of the peaks of III and V elements did not reveal the formation of incidental compounds. When etched InSb samples are stored in isopropanol (and less than 10 min in air, this is the time required to load the sample into the setup), indium oxide is also formed on the polished surface in addition to antimony oxide.

In turn, if the washing conditions are observed, the oxide of both main elements is formed (Table 8), with the exception of GaSb, the concentration of impurities from solutions on the surface of the samples reaches 2–3 at.% (Na, I). If the washing conditions were not met, the films were formed on all the samples.

Information about the stability of etching solutions over time is important (the effect of storage time on the etching rate, polishing ability, and so on). To establish this effect, we studied the changes in the etching rate observed for InSb, InAs, and GaSb in etchants of 9 mass.% I_2 in DMF (methanol) at room temperature. It should be noted that for InSb and GaSb these etchants are polishing, while the surface of the InAs wafers is covered with a film. As can be seen from Fig. 8, with an increase in the exposure time of the etching mixtures, the dissolution rates of the InAs crystals remain almost unchanged. For InSb and GaSb wafers in a 9 mass.% I_2 in DMF, the etching rates somewhat increase. The same

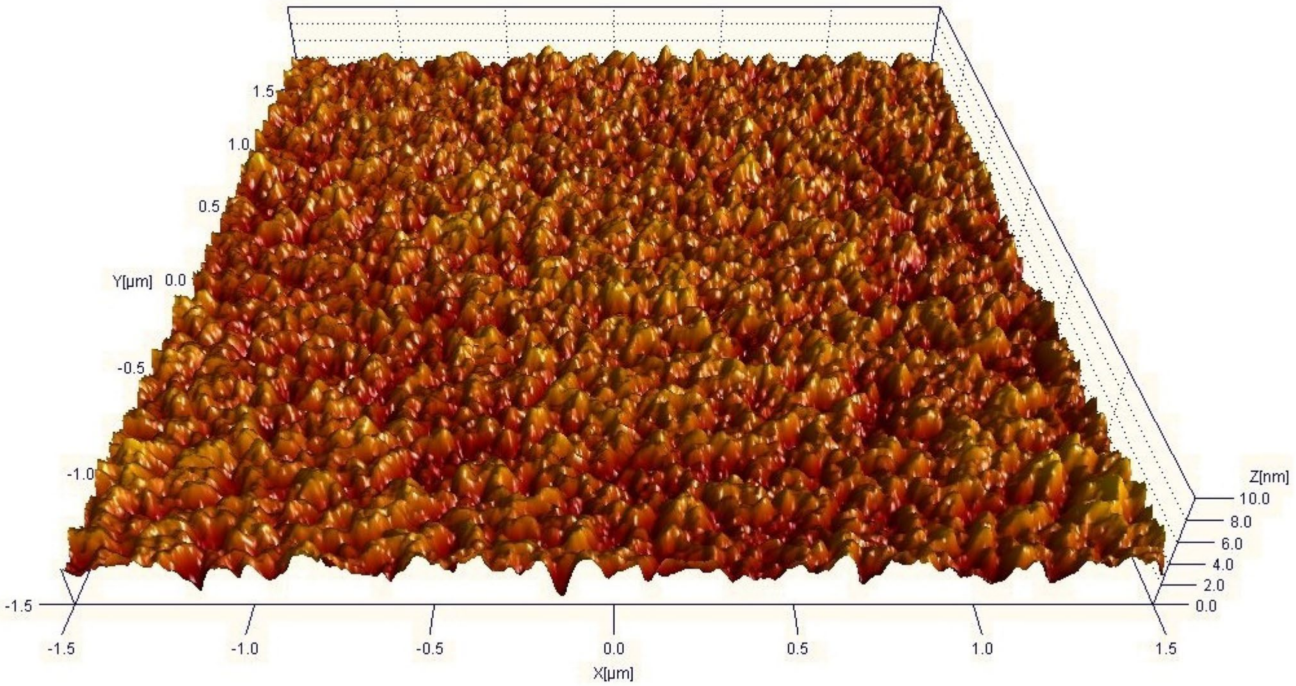

Fig. 7 AFM image of the GaAs crystals surface after CDP in a mixture of 12 mass.% I_2 in methanol

Table 6 Parameters of the surface roughness of GaAs and InSb single crystals after CDP treatment with I_2 + DMF (methanol) (roughness parameters for a 3 × 3-µm surface fragment)

Semiconductor	Etchant	Real surface area (µm^2)	R_a (nm)	*Rms* (nm)
GaAs	I_2 + methanol	9.0	0.6	0.8
InSb	I_2 + methanol	9.1	29.6	35.5
	I_2 + DMF	9.2	108.9	125.8

R_a average, or arithmetic average of profile height deviations from the mean line;

Rms (R_q) quadratic average or root mean square average of profile height deviations from the mean line

crystals in a solution of 9 mass.% I_2 in methanol behave differently; for InSb the polishing rate increases with time and then decreases, while for GaSb, the dissolution rate hardly changes. It should be noted that holding such solutions for the studied time does not affect the polishing properties. Therefore, such etchants can be used for chemical polishing for a long time after their preparation, which is another advantage. This should be taken into account in the practical use of the proposed etching compositions.

Based on the generalization of all the obtained experimental data, it was established that the process of chemical etching of the above plates in solutions of I_2 in DMF (methanol) should be carried out at a temperature of 290–297 K and $\gamma = 78$ min^{-1}. Research on etching processing is the first stage in our efforts in this field of the investigations. In the future, we plan to treat GaAs, GaSb, InAs, and InSb substrates by chemical polishing with different concentrations of HI-based solutions.

Conclusion

The kinetics and mechanism of chemical dissolution of single-crystalline GaSb and InSb in I_2 + DMF and I_2 + methanol solutions were investigated under reproducible hydrodynamic conditions. With an increase in the amount of I_2 in DMF, the dissolution rate of InSb, InAs, and GaSb crystals increases from 0.4 to 7.7 µm·min^{-1}. When these crystals are etched in solutions of I_2 in methanol, the dissolution rate is slightly higher—1.9–9.6 µm·min^{-1}. Whereas GaAs dissolves in I_2 + DMF (methanol), the etching rates are very low and do not exceed 1 µm·min^{-1}. To form a polished surface on InSb crystals, I_2 + DMF and I_2 + methanol solutions should be used. The same solutions can be used for selective etching of the GaSb surface. It is shown that as a result of CDP with solutions of I_2 in methanol, an ultrasmooth GaAs surface with parameters $R_a = 0.7$ nm is formed. The absence of chemical treatment products on the surface of the samples of mention above semiconductors indicates a properly developed treatment method.

Table 7 Surface analysis results of GaAs, GaSb, InAs, and InSb samples after treatment in I_2 + DMF (methanol) and ion etching

Sample	Etchant	Surface condition[a]	V/III (atomic ratio)	V Oxide/V elemental (atomic ratio)
GaAs	I_2 + DMF	Transparent film	3.06	1.36
	I_2 + methanol	Polished, mirror-like	4.24	0.80
	Ionic etching	Polished, mirror-like	1.38	0
GaSb	I_2 + DMF	Etch pits	2.72	0.95
	I_2 + methanol	Etch pits	5.23	1.02
	Ionic etching	Polished, mirror-like	1.02	0
InAs	I_2 + DMF	Film	0.83	0.36
	I_2 + methanol	Translucent film	1.15	0.43
	Ionic etching	Polished, mirror-like	0.67	0
InSb	I_2 + DMF	Polished, mirror-like	0.39	0.59
	I_2 + methanol	Polished, mirror-like	0.45	0.71
	Ionic etching	Polished, mirror-like	0.63	0

[a] Optical microscope NU-2E (Carl Zeiss)

Table 8 Surface analysis results of GaAs, GaSb, InAs, and InSb samples after treatment in I_2 + DMF and ion etching when the whashing conditions are not observed

Sample	Etchant	V Overall/III atomic ratio	V Oxide/V elemental (atomic ratio)	III Oxide/ III elemental (atomic ratio)
GaAs	I_2 + DMF	6.40	0.56	0.67
	Ionic etching	1.38	0	0
GaSb	I_2 + DMF	4.24	1.05	0
	Ionic etching	1.02	0	0
InAs	I_2 + DMF	1.21	0.41	0.16
	Ionic etching	0.67	0	0
InSb	I_2 + DMF	0.53	0.40	4.79
	Ionic etching	0.63	0	0

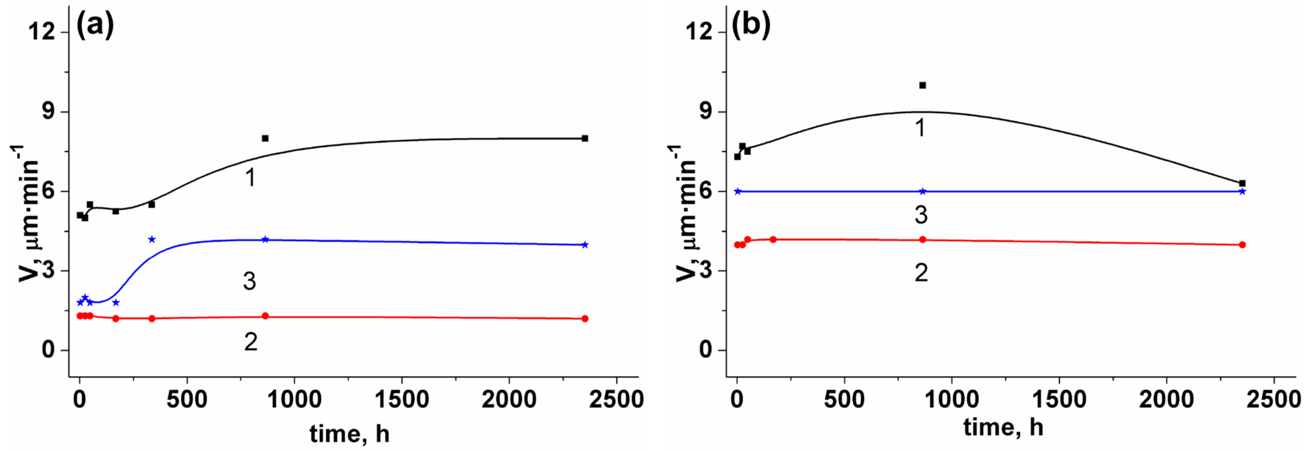

Fig. 8 Dependences of the dissolution rate (µm·min^{-1}) on the exposure time of solutions of **(a)** 9 mass.% I_2 in DMF and 9 **(b)** mass.% I_2 in methanol: **1**—InSb; **2**—InAs; **3**—GaSb. (T = 290–295 K, γ = 78 min^{-1})

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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